



Short communication

A novel, easily synthesized, anhydrous derivative of phosphoric acid for use in electrolyte with phosphoric acid-based fuel cells

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HIGHLIGHTS

- ▶ A phosphoric acid-based fuel cell liquid electrolyte for $T > 200^\circ\text{C}$ without pressure.
- ▶ An unhumidified electrolyte of H_3PO_4 , saturated with a new silicophosphoric acid.
- ▶ Polarization curves at 226°C with OCV $> 0.95\text{ V}$, and current densities to 1.0 A cm^{-2} .
- ▶ Fuel cell of exceptional current efficiency – burns almost all the available fuel.

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ABSTRACT

We build on the success of phosphoric acid as a fuel cell electrolyte, by designing a variant of the molecular acid that provides increased temperature range without sacrifice of high temperature conductivity or open circuit voltage. This is achieved by introduction of a hybrid component, based on silicon coordination of phosphate groups, which prevents decomposition or water loss to 250°C , while enhancing free proton motion. We report conductivity studies to 285°C and full H_2/O_2 cell polarization curves to 226°C with careful monitoring of fuel consumption. The current efficiency we report (current density per unit of fuel supplied per sec) is as high as the highest on record. A power density of 184 mW cm^{-2} is achieved at 226°C with hydrogen flow rate of 4.1 ml min^{-1} .

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1. Introduction

The phosphoric acid fuel cell is known as one of most researched, and commercially most advanced types of fuel cell [1,2]. Initially developed as a liquid electrolyte device, prone to leaking and ionic shorts, it is now being refined, by incorporation of H_3PO_4 in polymeric materials [3] such as polybenzimidazole, into a very promising and cost-competitive alternative [4] to the Nafion fuel cell [5,6]. An advantage it holds over its Nafion rival is the higher temperature range of operation permitted by the electrolyte. It can be used up to 160°C before water loss, to form pyrophosphoric acid, leads to reduced conductivity and poorer performance. The range may be extended by elaborate humidification and pressurization provisions, which of course also increase the expense and failure-probability of the system. The water management

problem remains a barrier to the full commercialization of this type of fuel cell. Any modification of the electrolyte that could extend its operating temperature range and reduce its dependence on the presence of some water, without reducing its other favorable characteristics would be of great interest.

Here we describe an inexpensive, easily synthesized, modification of H_3PO_4 (presumed to be a binary solution with a new more complex acid) that extends the temperature range of the phosphoric acid fuel cell to 250°C , while improving its operating fuel efficiency considerably. To our knowledge, the current efficiency ($= i/i_{\text{theoretical}}$, i = current) obtained with the electrolyte we will describe, is higher than that of any other type of fuel cell operating at 1 atm. pressure. Its voltage efficiency is also comparable to (somewhat better than) that of the reported phosphoric acid-based fuel cells. We describe only the first stage of this development, viz., the liquid electrolyte and its fuel cell performance, leaving the important second stage – development of a membrane based on proper incorporation of the liquid into a robust polymer host – to future reports.

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2. Chemistry

The additive is a derivative of phosphoric acid in which phosphoric acid is combined with silicon to form a silicophosphoric acid which probably has multiple molecular forms – yet to be fully resolved. Initially it was thought to be a substantial component of the electrolyte, but later work suggests that is a minor but temperature-dependent component that stabilizes the phosphoric acid against loss of more than a small amount of water. Its possible molecular form will be discussed briefly below. It is the subject of continuing investigation.

The electrolyte is prepared by reacting SiCl_4 with anhydrous phosphoric acid obtained by fusion of the dry crystalline form ($T_m = 42^\circ\text{C}$). The reaction is carried out under mild conditions, under gentle flow of nitrogen gas, initially 45°C (T_b of SiCl_4 is 57°C) and continuing with gradually rising temperature (reaching 100°C) for 3 h until the liquid is saturated with reaction products (becoming creamy in color due to a fine precipitate of solid material), followed by gradually increase of temperature to 270°C over 1 h that establishes an equilibrium content of $\text{H}_4\text{P}_2\text{O}_7$. The H_3PO_4 -insoluble components can be increased in quantity by extending the reaction time. The fuel cell performance has been evaluated in the presence of the stable suspension of solid silicophosphoric acid, called here SiPOH for convenience, which is believed to be essential for maintaining electrolyte properties. The solid is of highly disordered character according to X-ray diffraction patterns [7] to be discussed elsewhere [8].

Both the liquid and the stably suspended solid are strongly acidic in character. The solid material contains Si in six-coordination [8]. It has interesting properties including the ability, on solution in water and extended evaporation, to produce a clear deformable polymeric solid that has stability up to 140°C at 1 atm, and conductivity in excess of that of pressurized Nafion. This rubbery solid or gel-like material will be described in more detail elsewhere, but its conductivity, measured in the piston cell described recently [9], is included in Fig. 1.

3. Results

3.1. Conductivity

The presence of SiPOH and an equilibrium content of $\text{H}_4\text{P}_2\text{O}_7$ in the phosphoric acid, leads to an increase in electrolyte viscosity. Nevertheless, above 150°C the electrolyte conductivity, determined using a twin electrode dip-type cell of cell constant 1.83 cm^{-1} , is superior to that of pure H_3PO_4 as shown in Fig. 1. This is presumably due to a superior “free” proton contribution at high temperatures. The conductivity is reversible up to 285°C . Tested at a constant 250°C , the conductivity remained invariant within the temperature control fluctuations over a 24-h period, and over a 48 h at 230°C , so loss of water has been greatly diminished, and in an operating fuel cell (producing water) would not be of consequence.

In Fig. 1, comparison is made with anhydrous H_3PO_4 , Nafion, and with the rubbery polymer obtained by hydrating the solid products of the reaction (to be described separately). Data for the diethylmethylammoniumtriflate $[\text{DEMA}^+][\text{OTf}^-]$ [10] used in a recent protic ionic liquid fuel cell [11, 12], are shown as a dashed line. Even at 25°C , the conductivity is still as good as that of the best ambient temperature protic ionic liquid fuel cell electrolyte.

3.2. Fuel cell performance

The performance of our modified H_3PO_4 liquid electrolyte, studied in the same Teflon sandwich cell with E-Tek gas diffusion electrodes, described in previous publications [13], is shown in Fig. 2. Note that we are able to operate smoothly at temperatures as high as 226°C , and could go higher if not for the materials limits on tubular and machined components of the cell. Using unhumidified gases, we have been able to draw currents of 1 amp cm^{-2} , with open circuit voltages (OCV) of nearly 1.0 V. This OCV is only 0.12 V

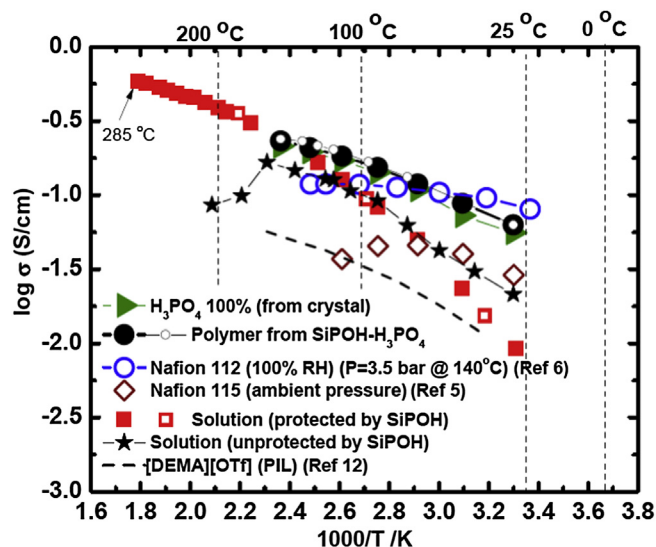


Fig. 1. Ionic conductivities of the new SiPOH-stabilized electrolytes compared with various fuel cell electrolytes, including Nafion. Data from the present work are in solid symbols for heating runs and smaller open symbols for cooling runs, to show reproducibility. Star symbols show the conductivity of the new electrolyte after prolonged centrifuging to remove the SiPOH suspension. Only the heating data are shown. The conductivity of the protic ionic liquid DEMA triflate (ref. [10]), used in a recent fuel cell membrane (refs. [11,12]), is shown as a dashed line for comparison.

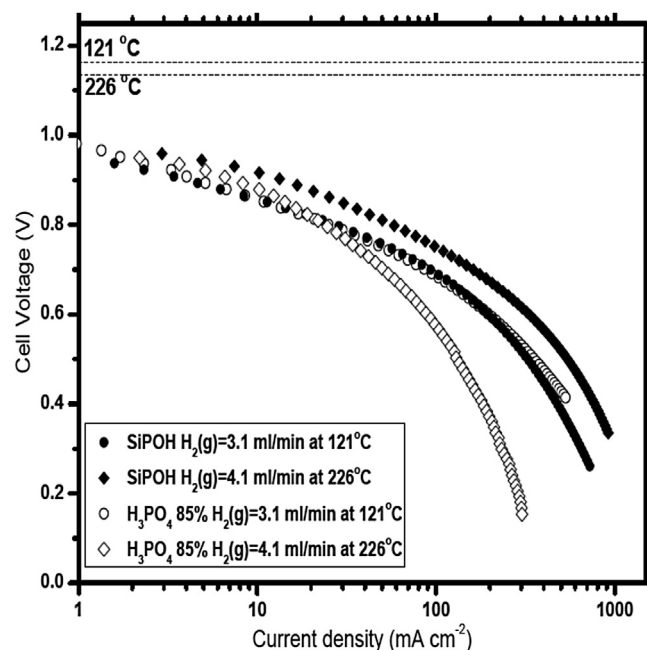


Fig. 2. Tafel plots (IR corrected) for fuel cell performance, using the new SiPOH-stabilized phosphoric acid, compared with performance using the commercial standard, H_3PO_4 , 85%. The experiments used identical Teflon fuel cell blocks with identical E-Tek electrodes, and the same flow rates of H_2 and O_2 for each electrolyte at each temperature (see Table 1 for details). Flow rate for $\text{O}_2 = 2 \times$ flow rate for H_2 . Note the high OCV, and $\sim 1\text{ amp cm}^{-2}$ current, obtained at 226°C .

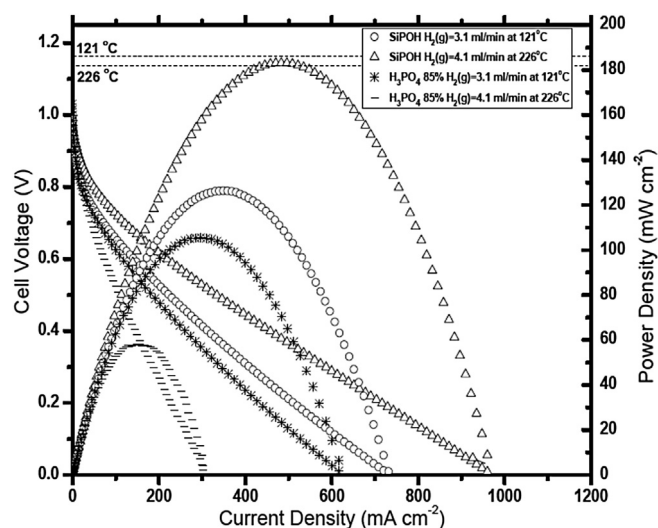


Fig. 3. Polarization curves (linear current and no IR correction), and the corresponding power densities, for SiPOH-stabilized anhydrous H_3PO_4 , and H_3PO_4 (85 wt%), electrolytes at different temperatures up to 226 °C.

below the thermodynamic value for that temperature, and is somewhat higher than that obtained with the standard 85 wt% phosphoric acid electrolyte (also shown in the figure).

The power outputs for the SiPOH-stabilized electrolyte at the two temperatures of Fig. 2 are shown in Fig. 3. The currents, both at (i) maximum power and (ii) where cell voltage vanishes in the uncorrected polarization curve, are shown, along with open circuit voltage, voltage at maximum power, and other performance characteristics, in Table 1.

An important aspect of the fuel cell performance with the present electrolyte is the fuel usage efficiency. This is a feature that is discussed in the literature less than one might expect. It is monitored by the hydrogen flow rate at maximum current. Most workers adjust the fuel flow rates to maximize the current, and then often report this flow rate, typically $10\text{--}50\text{ ml min}^{-1}$ without discussing

the relation of fuel supplied to current obtained. This is understandable as it is usually not an encouraging number. However in the present case, the cell is burning nearly all the fuel supplied. We provide in Table 1, the current efficiency (defined as $(1/2 \text{ the moles } \text{H}_2 \text{ supplied per second})/(\text{Faradays of electricity flowing per second})$), both at the peak power condition. A second value based on the current flowing when the cell voltage (without IR correction) vanishes, is sometimes made, and in the case of our cells may approach 100%, but the first metric is the more relevant. In a cell of ideal design, such that the polarization curve is of rectangular form [14], the two would be the same.

We include in Table 1 the current efficiencies reported by various workers for different types of fuel cells, and also calculate it in cases where both hydrogen flow rate, and current at maximum power, were reported but no current efficiency calculation was made. The current efficiency, when the standard 85% H_3PO_4 electrolyte was used in our cell, was high, consistent with experience of the favored electrolyte. Indeed, at 121 °C, it was as high as with the SiPOH-stabilized electrolyte. However a major difference arose when the higher temperature range was explored, the SiPOH-stabilized electrolyte reaching 1 amp cm^{-2} without any sacrifice in cell voltage. The power output at this temperature, shown in Fig. 3, reached a very favorable 184 mW cm^{-2} , and this number could clearly be improved upon with more attention to cell design (to more closely approach the ideal rectangular polarization curve [14]).

The voltage efficiency is also presented in Table 1, using two alternative definitions. The first is simply the $[\text{OCV/theoretical emf}] \times 100$ at the temperature of measurement, while the second (and more relevant one) is that based on the voltage at the power maximum – obviously a much smaller number. Again, the SiPOH-stabilized electrolyte is yielding favorable numbers relative to other cells for which the data are available. Again the advantage of high temperature operation is to be stressed.

We should recognize that our favorable voltage efficiencies, which would further improve with cell designs that produce a slower crossover to mass transport control, might be enhanced by the fact that our electrolyte thickness (3 mm to permit exchange of liquid electrolyte without change of any other parameters) is

Table 1
Fuel cell performance conditions and metrics.

| | Operating temp (°C) | H_2 flow rate (ml min^{-1}) | Max. current dens (mA cm^{-2}) | Current dens P_{max} (mA cm^{-2}) | Current effc % | Current effc % at P_{max} | Voltage effc % (OCV) | Voltage effc % at P_{max} | Reference |
|---------------------------------------------------------|---------------------|-------------------------------------------------|-------------------------------------------|-------------------------------------------------------|----------------|------------------------------------|----------------------|------------------------------------|-----------|
| Nafion 115 | 30.0 | 20.0 | 660.0 | 540.4 | 25.1 | 20.6 | 73.1 | 34.9 | (a) |
| Nafion 117- polypropylenecomposite (70:30 weight ratio) | 22.0 | 100.0 | 700.0 | — | 5.3 | — | 57.2 | — | (b) |
| Nafion/inorganic composit membrane RH = 50% | 120.0 | >270 | 580.0 | 433.6 | 1.7 | 1.2 | 81.8 | 35.8 | (c) |
| Pristine Nafion membrane | 60.0 | 300.0 | 1800.0 | 1208.5 | 4.6 | 3.1 | 79.4 | 39.8 | (d) |
| Molten carbonate fuel cell (fluidized bed electrode) | 650.0 | 10 (O_2) | 115.6 | — | 8.8 | — | 29.1 | — | (e) |
| [dema][TfO] in Sulfonated Polyimide | 30.0 | 120.0 | — | 450.0 | — | 2.9 | 67.8 | 29.3 | (f) |
| | 120.0 | 12.0 | — | 190.0 | — | 12.1 | 64.6 | 28.2 | (f) |
| | 140.0 | 12.0 | — | 50.0 | — | 3.1 | 59.7 | 35.7 | (f) |
| Phosphoric acid 85% (cell area 0.5 cm^2) | 121.0 | 3.1 | 622.0 | 299.0 | 76.3 | 36.4 | 88.7 | 30.7 | This work |
| | 226.0 | 4.1 | 303.0 | 115.0 | 28.0 | 14.4 | 85.7 | 32.9 | This work |
| SiPOH (cell area 0.5 cm^2) | 121.0 | 3.1 | 731.0 | 345.0 | 89.7 | 38.4 | 85.4 | 33.0 | This work |
| | 226.0 | 4.1 | 966.0 | 477.0 | 89.6 | 44.3 | 85.4 | 33.8 | This work |

All results are given based on 1 bar pressure and cell area of 1 cm^2 .

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(b) Sabit Adanur et al., NTC Project: F04-AE01, National Textile Center Annual Report: November 2006.

(c) C. Wang, E. Chalkova, J.K. Lee, M.V. Fedkin, S. Komarneni, S.N. Lvov, J. Electrochem. Soc. 158 (6) (2011) B690–B697.

(d) W. Zhao, T. Haolin, Z. Huijie, L. Ming, C. Rui, X. Pan, P. Mu, J. Membr. Sci. 421–422 (2012) 201–210.

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(f) S.-Y. Lee, A. Ogawa, M. Kanno, H. Nakamoto, T. Yasuda, M. Watanabe, J. Am. Chem. Soc. 132 (2010) 9764–9773.

greater than that of the common membrane. This would inhibit fuel crossover effects that diminish cell voltage. This might invalidate comparisons with some membranes. The cell was designed so that, by simple exchange of liquid electrolyte, multiple comparisons of the current flowing and the voltage (both open circuit and that at the power maximum) could be made for different protic ionic liquids [13], though this feature could not be utilized in the present study because of the importance of the solid SiPOH suspension to the function of the system.

The challenge now is to incorporate this electrolyte in a polymer membrane without low temperature aqueous processing which evidently produces chemical modifications (witness the hydrated polymer with extraordinary conductivity shown in Fig. 1, the fuel cell performance of which will be described in separate publications). Because it is of more acid character than hydrated H_3PO_4 , the SiPOH-stabilized electrolyte should be more firmly retained in a polybenzimidazole membrane than H_3PO_4 (due to the larger proton transfer energy to the basic nitrogen [15, 16]), so this type of membrane is an obvious first choice. Like the structural characterization of the SiPOH molecule(s), we defer such membrane evaluations to subsequent papers.

4. Discussion

Phosphorus–silicon–oxygen combinations incorporating H_3PO_4 have been used previously to produce proton-conducting electrolytes for fuel cell applications. Matsuda et al. [17] have described phosphosilicate gel powders and H_3PO_4 -impregnated porous silica gel powders that have moderately high conductivity and stability at elevated temperatures, but they are made by sol-gel processes and must have chemical constitutions that are rather different from the anhydrous systems of the present work. A more closely related, but partly organic formulation, has been that of Nida et al. [18], but the material of Nida et al., in which dimethyldichlorosilane was reacted with phosphoric acid, was prepared as a precursor material for low-melting glass formulations. The molecular silicophosphates described to date have been very large species e.g. the 25 oxygen compound $\text{Si}_5\text{O}(\text{PO}_4)_6$ [19] and related species of ref. [20], for which little or no solubility in H_3PO_4 would be expected.

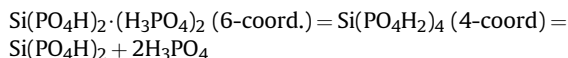
Our active compounds are evidently of less complex character, resulting in an H_3PO_4 -soluble material, probably of temperature-variable form, that strongly influences the properties of the H_3PO_4 -based electrolyte.

One possible form, which high level gas phase electronic structure calculations at 298 °C (ORCA program package – using Density Functional Theory (DFT) with B3LYP/G (Becke, three-parameter, Lee-Yang-Parr) basis sets plus polarization and diffusion functions) have shown to be stable, and also of stronger acid character than H_3PO_4 itself, is $\text{Si}(\text{PO}_4\text{H})_2$, with Si coordinated as in Fig. 4. Calculations were done in parallel mode using a cluster of 8

nodes, and are comparable to, though somewhat more quantitative than, those of Schaeffer and coworkers [21] on H_3PO_4 .

$\text{Si}(\text{PO}_4\text{H})_2$ is a relatively small molecule, consistent with the high conductivity of the liquid at 280 °C. Such species are not known in the solid state, however, and are likely to be present only as a consequence of temperature-induced coordination number changes from the six-coordinated state known for most solid forms of silicophosphates [19,20] (and also identified in NMR studies [8] of the solid that forms as a component of the equilibrium described below).

One of a variety of possible equilibria between solid and liquid forms could be that depicted in the following scheme, the right hand side being favored by higher temperatures.



These forms are related by the redistribution of protons, and tilting of the orthophosphate groups. Such an equilibrium would involve minimal changes in density, thus accounting for the stability of the suspension which can only be separated out by prolonged centrifugation. The molecular level characterization of the silicophosphoric acid is not needed to appreciate the fuel cell performance, so will be left for later articles [8]. We note again, though, that the white quasi-solids that form a suspension when the reaction that produces the SiPOH electrolyte is continued, has silicon in six-fold coordination [8] presumably with phosphate oxygen, as in the above scheme. The ambient temperature liquid state does not contain detectable ^{29}Si [8], so the constitution of the high temperature solution, which need not be known for the present report, is uncertain at this time and is the subject of continuing study.

We assume that the good performance of the present electrolyte is partly a consequence of the higher temperatures that can be reached, but partly also a consequence of some favorable modification of the surface tension that improves the complex kinetics at the three-phase boundary (gas/catalyst/electrolyte). This is a subject for future investigations, in which comparative surface tension measurements will be included.

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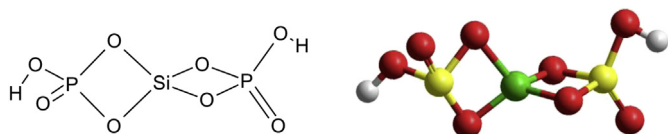


Fig. 4. One of the possible structures of siphoric acid monomer shown in Sticks (left) and Balls and Cylinders (right) formats. Silicon (green), hydrogen (white), oxygen (red), and phosphorous (yellow). The double edge-sharing, fourfold coordination, would constitute an unusual silicon coordination, made possible by the intense oxygen polarization by P(V). Other possibilities involving corner-linked phosphates and edge-shared phosphate octahedra are noted below and will be considered elsewhere. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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